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(54) Electroplating solutions

(57) An acid copper electroplating composition comprising an aqueous solution of an acid and a copper salt, wherein at least one carrier compound, a water-

soluble, mercapto-containing organic brightener compound and a leveller compound which comprises an organic compound containing single or multiple charged centres are present.

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Description

[0001] This invention relates to improved copper electroplating solutions and, more particularly, to improved acid copper electroplating solutions and the use of new carriers, brighteners and levellers, as well as molecules, that combine carrier/brightener and carrier/leveller functionality.

[0002] Copper electroplating baths are used in a variety of industries. In the semiconductor industry in particular, there is an increasing need for such baths to meet decreasing device feature size, increasing wafer size and high yield. Various proprietary electroplating bath chemistries are commercially available that claim success with regards to the copper metallisation process. Ideally, the bath chemistry should help to fill with copper small yet high aspect ratio trenches and vias, for example less than $0.18 \mu\text{m}$, and an aspect ratio greater than 5, to obtain uniform and void free plating while maintaining high production rates. The plating bath chemistries should also be relatively chemically stable, less corrosive and easily monitored and replenished.

[0003] Copper sulphate and sulphuric acid are the basic constituents of the acid copper electroplating bath chemistry. Organic additives such as carriers, brighteners, levellers and combinations of these can assist in providing a plating bath which can fill the small and high aspect ratio trenches and vias without voids or seams. As-plated copper deposits can be of uniform thickness and fine grain size, and highly "111" crystal orientated.

[0004] Carriers typically are water-soluble polymers containing $-(\text{CH}_2)_n-\text{O}-$ where $n = 1$ to 3 or branched derivatives in the main chains. Carriers can form a monolayer film at the cathode surface, which is a barrier to the diffusion of Cu^{+2} ions to the surface and polarises the cathode. The proper polarisation of the cathode is a prerequisite for producing fine and orientated grain structure. However, carriers tend to decompose into lower molecular fragments at both the cathode and the anode, and lose polarisation effectiveness. As such, carriers with high stability are desired.

[0005] Brighteners not only produce fine and orientated grain structure for the as-plated deposits but also provide better chemical stability and solubility in the electroplating bath. Brighteners are typically water-soluble sulphonic acids containing mercapto and/or thio groups. US Patent Specification No. 5,151,170 discloses a brightener that consists essentially of the hydrogen peroxide oxidation product of a dialkylamino-thioxomethylthioalkanesulphonic acid wherein each alkyl and alkane group individually contains 1 to 6 carbon atoms. They can produce fine copper deposits by masking the preferential growth sites/planes. However, current brighteners can suffer from poor stability, oxidation by air and electrochemical oxidation at the anode, as well as catalytic decomposition at the copper surface. The decomposed products are often detrimental to copper deposition properties.

[0006] Levellers play a key role in void and seam free trench filling, i.e., superfilling or bottom-up filling. The deposition rate needs to be much faster at the bottom of the features than on the side wall and shoulder of the trenches and vias. As such, different molecular size levellers are employed to tailor different generation (or size) of trenches and vias. The large molecular size is usually preferred for the filling of larger trenches and vias since the diffusion of the levellers towards the bottom of trenches is much slower, which in turn results in extremely low leveller flux at the bottom and promotes bottom-up filling or superfilling. However, the larger molecular size can eventually block the openings and prevent the copper ions from entering the trenches. This consequently creates voids when the size of the trench and vias is greatly reduced, for example of the order of $0.1 \mu\text{m}$.

[0007] Various chemically combined brightener/carrier and/or leveller/carrier can further enhance these functions and goals. The as-plated copper deposits can complete self-annealing process in several hours to have a stable microstructure at room temperature.

[0008] US Patent Specification No. 5,051,154 discloses an aqueous electroplating solution comprising at least one soluble copper salt, an electrolyte and at least one organic additive capable of modifying the charge transfer overpotential of the solution in an amount sufficient to shift the overpotential by at least 150 millivolts and being independent of solution agitation. This prior specification discloses the use of a wetting agent as a component additive in the system capable of modifying the charge transfer overpotential. Additional additives can include a brightener along with the wetting agent and this can be selected from the group consisting of n , n -dimethyl-dithiocarbamic acid - (3-sulphopropyl) ester, 3-mercapto-propylsulphonic acid (sodium salt); carbonic acid-dithio-o-ethylester-s-ester with 3-mercapto-1-propane sulphonic acid (potassium salt); bisulphopropyl disulphide; 3-(benzthiazolyl-s-thio) propyl sulphonic acid (sodium salt); and pyridinium propyl sulphobetaine. The three component additive may also include levellers such as those selected from the group including 1-(2-hydroxyethyl)-2-imidazolidinethione; 4-mercaptopyridine; 2-mercaptothiazoline; ethylene thiourea; thiourea; and alkylated polyalkyleneimine.

[0009] The invention is concerned with the provision of an improved acid copper electroplating bath compositions and methods for preparing them, which generally overcome the problems disclosed above with existing compositions.

[0010] In accordance with the invention, there is provided an acid copper electroplating composition comprising an aqueous solution of an acid and a copper salt, wherein at least one carrier compound, a water-soluble, mercapto-containing organic brightener compound and a leveller compound which comprises an organic compound containing single or multiple charged centres are present.

[0011] In a separate aspect of the invention there is provided a method for copper plating or metallisation of advanced interconnects (less than 0.18 microns and having an AR (Aspect Ratio) greater than 6) comprising immersing a substrate intended for advanced interconnects into the copper electroplating composition and conducting an electrochemical deposition process.

[0012] In a typical known acid copper electroplating bath, an acid and a copper salt are employed. The acid is typically sulphuric acid while the copper salt can be selected from copper sulphate, copper acetate, copper fluoborate, cupric nitrate and copper pyrophosphate. Additional inorganic additives can include both chloride and alkaline species. The chloride can enhance cathode surface adsorption of organic additives such as the carrier and improve the oxidation of the anodes to improve plating efficiency. Alkaline species such as ammonium hydroxide are added to reduce the acidity and corrosivity of the bath solution. Chloride can be added in an amount of about 20 to 100 parts per million parts water in the bath, while the alkaline is added in an amount necessary to reduce the pH of the solution.

[0013] In the invention, the acid copper electroplating solution composition advantageously contains from about 50g to about 250g of copper salt per litre of water and about 60g to about 250g of sulphuric acid per litre of water.

[0014] In addition to sulphuric acid, copper salt, and inorganic additives disclosed above, one or more of organic additives such as carriers, brighteners, levellers, and combinations of these may also be employed to obtain high throwing power to fill the small and high aspect ratio trenches and vias.

[0015] The carriers used in this invention can comprise conventional ones used in the art, for example polyethylene glycol and poly(ethylene oxide), and polysaccharides. The polysaccharides may comprise simple sugars such as fructose and glucose linked by glycosidic bonds, for example starch, cellulose, amylopectin and amylose.

[0016] The brighteners useful in the invention possess both stability and solubility in the copper electroplating bath. The brighteners include both water soluble mercapto-containing organic compounds and other organic sulphides. Representative examples include but are not limited to N-methylallyl-N'-methylthiourea; tetramethylthiuram disulphide; ethylethylthiomethyl sulphoxide; ammonium diethyldithiocarbamate; dimethyl-2-thioxo-1,3-dithiole-4,5-dicarboxylate; 3-mercapto-1-propanesulphonic acid sodium salt; 3-mercapto-1-propanesulphonic acid; bis (2-mercaptoethyl) sulphide; ethylene trithio carbonate; ethanethiol; 2-mercaptoethanol; monothioglycerol (1-thioglycerol); 1,2-ethanedithiol; and thiodiethanol. The most preferred brighteners are ammonium diethyldithiocarbamate, 3-mercapto-1-propanesulphonic acid sodium salt, and its free acid form. 3-Mercapto-1-propanesulphonic acid is prepared from 3-mercapto-1-propanesulphonic acid

sodium salt by an ion-exchange process using cation ion-exchange resins such as Dowex DR2030 (20-30 mesh), Dowex HCR-W2 (16-40 mesh), Dowex 50Wx8-100 (50-100 mesh, 1.7 meq / mL, 0.80 g / mL), and Dowex 50Wx8-200 (100-200 mesh, 1.7 meq / mL, 0.80 g / mL). The sodium level can be reduced to a few ppm from about 1500 ppm in original 1 wt. % aqueous solution. Both a packed column with ion-exchange resin and a reaction flask approach using ion-exchange resin can remove sodium to low ppm levels.

[0017] The need for a sodium-free brightener is important in avoiding sodium contamination of the copper deposited thin layer. The 3-mercapto-1-propanesulphonic acid can be prepared by both ion-exchange column and in a reaction flask, and sodium removal efficiency was better than 99% for both methods. This is important regarding bath life as the buildup of sodium in the bath over time would require the bath to be dumped and replenished once the sodium level becomes unacceptably high.

[0018] The levellers useful in this invention possess single or multiple positively charged centres that will form single or multiple positively charged sites after protonation in the acidic conditions of the bath. In this invention, the levellers are divided into three groups - polymeric levellers, low molecular weight levellers, and organic dyes.

[0019] Representative examples of polymeric levellers include but are not limited to polyethylenimine, 80% ethoxylated; poly(allylamine); poly(allylamine hydrochloride); polyaniline, sulphonated, 5 wt. % in water, 75 mole % sulphonated; poly[bis(2-chloroethyl)ether-alt-1,3-bis[3-(dimethylamino)propyl]urea, quaternized; poly[N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-1,6-hexanediamine-co-2,4-dichloro-6-morpholino-1,3,5-triazine]; polyacrylamide; poly(acrylamide-co-diallyldimethylammonium chloride); poly(diallyldimethylammonium chloride); poly(melamine-co-formaldehyde), partially methylated; poly(4-vinylpyridine), 25% cross-linked; poly(1,2-dihydro-2,2,4-trimethylquinoline). The most preferred polymeric levellers are poly[bis(2-chloroethyl)ether-alt-1,3-bis[3-(dimethylamino)propyl]urea, quaternized, and poly(diallyldimethylammonium chloride)].

[0020] Representative examples of low molecular weight levellers include but are not limited to N-containing acyclic systems, N-containing five-membered heterocyclic systems, and N-containing six-membered heterocyclic systems. Most of them also contains mercapto-, sulphide, or disulphide functionalities. Representative examples of N-containing acyclic systems include 2,5-dithiobiurea, dithiooxamide, 1-phenyl-2-thiourea; and diethylenetriamine. The most preferred one is diethylenetriamine. Representative examples of N-containing five/six-membered heterocyclic systems include p-xylenebis(tetrahydrothiophenium) chloride, 2-thiohydantoin, pseudo thiohydantoin, (R)-(-)-thiazolidine-4-carboxylic acid, 3-(2'-thiopyridinium) propyl sulphate, 2,2'-dipyridyl disulphide, 4,4'-dipyridyl disulphide,

thionicotinamide, 4-(trifluoromethyl)-2-pyrimidinethiol, 2-mercapto-4-methylpyrimidine hydrochloride, 5-phenyl-1 H-1,2,4-triazole-3-thiol, 5-(4'-pyridyl)-1 H-1,2,4-triazole-3-thiol, 2-amino-6-purinethiol, 4-amino-5-(4'-pyridyl)-4 H-1,2,4-triazole-3-thiol, diethyl heptadecyl imidazolinium ethylsulphate, hexamethylenetetraamine, 1,3-bis(3-pyridylmethyl)-2-thiourea, 2,4-diamino-6-mercaptopyrimidine hemisulphate, dithiouracil, 4,5-diamino-2,6-dimercaptopyrimidine, 4,5-diamino-6-hydroxy-2-mercaptopyrimidine hemisulphate hydrate, 4(5)-imidazolidithio-carboxylic acid, 2-mercapto-5-benzimidazolesulphonic acid, sodium salt dihydrate, 2-thiouracil, trithio cyanuric acid, (2-pyrimidylthio) acetic acid, 7-trifluoromethyl-4-quinolinethiol, 5-carboxy-2-thiouracil, 1 H-1,2,4-triazole-3-thiol, 1-phenyl-1 H-1,2,4-triazole-5-thiol, N,N'-ethylene thiourea, and 2-mercapto benzothiazole. The most preferred one is thionicotinamide.

[0021] Representative examples of organic dyes include but are not limited to Bismarck Brown Y ($C_{18}H_{15}N_8 \cdot 2HCl$), Chicago Sky Blue 6B ($C_{34}H_{24}N_6O_{16}S_4Na_4$), and Acid Violet, for example Acid Violet 7 ($C_{20}H_{16}N_4O_9S_2Na_2$).

[0022] The organic additives are constantly consumed due to breakdown and oxidation in the electroplating process. The consumed additives are generally compensated for by a replenishing process to maintain constant bath chemistry. Numerous consumption/replenishment cycles may proceed before a complete replacement of the plating bath is necessary. As a result of this process, there is an accumulation of contaminants which can be a critical problem. The contaminants may interfere with the functioning of organic additives and may cause inconsistent plating that is unacceptable to the semiconductor industry.

[0023] It has been found that removal of organic additives can be accomplished with activated carbon such as type 4040 and DCL activated carbon available from Bameby Scientific Corp. The bath can be filtered through an activated carbon bed and returned to the plating bath without the need for dumping and restocking the plating bath. The increased number of cycles without having to remake the bath improve effectiveness and economics of the plating process.

[0024] This consumption and breakdown of the plating bath additives will result in the need for replenishment of these additives. An accurate determination is needed in-situ and feedback provided fairly rapidly to enable efficient use of baths by semiconductor fabs. The criteria for this analysis include the ability to separate bath components, minimum detection limits, measurement time, accuracy and repeatability and the complexity and frequency of calibration and maintenance. Electrochemical analytical techniques such as cyclic voltammetric stripping (CVS), AC-cyclic voltammetry (AC-CV), AC impedance spectroscopy (AC-IS) and pulsed cyclic galvanostatic analysis (PCGA) have been employed. CVS is generally preferred as it provides relatively high

measurement accuracy and fast test results while not generating waste. High performance liquid chromatography (HPLC) is also employed as it offers the advantage of allowing quantitative measurement of contaminants and determination of break-down additives.

[0025] The invention further comprises the use of molecules that combine brightener/carrier and carrier/leveller functionalities. The combination of brightener/carrier is typically a monomeric to polymeric protein chain where the chain is linked by sulphide and disulphide bridges. The combination of carrier/leveller can help improve the stability of the leveller while simplifying the bath by reducing the number of organic additives. Such materials can be poly[bis(2-chloroethyl)ether-alt-1,3-bis[3-(dimethylamino)propyl]urea, quaternized, and poly(melamine-co-formaldehyde), partially methylated.

[0026] The carrier of the invention may be added in an amount ranging from about 2 to about 1000 parts per million parts water. The leveller may be added in an amount of about 2 parts to about 1000 parts per million parts of water in the electroplating solution.

[0027] The brightener may be added in an amount ranging from about 5 parts to about 100 parts per million parts water. When the combination carrier/brightener is employed, it is added in an amount ranging from about 5 to about 100 parts per million parts water. The combination carrier/leveller when employed may be added in an amount ranging from about 2 to about 1000 parts per million.

[0028] Other additives that are found in the baths include wetting agents such as carboxylic acids and antioxidants. Carboxylic acids such as citric acid improve wetting ability of the cathode and provide better adsorption of the organic additives to the cathode. Typically, these are added in a range of about 2 to about 1000 parts per million parts water in the bath.

[0029] Brighteners tend to be oxidised in the vicinity of the anode during and without plating. Oxidised brighteners lose their functionality and cause an inconsistent plating rate and poor quality of the as-plated object. The oxidising agents near the cathode are typically hydrogen peroxide and oxygen. Continuously purging the bath solution near the anode side with an inert gas is preferred as this will generally expel oxygen out of the solution.

[0030] The additive packages of the invention may be added to the aqueous acid copper electroplating bath either individually or as combinations depending upon the type of substrate being plated.

[0031] The plating solutions of this invention are used in a conventional manner. They are preferably used at room temperature or higher temperature. During plating, the bath solution is preferably agitated by inert gas, air sparger or by mechanical means. The plating current density is preferably between 3 mA/cm² and 40 mA/cm² depending on aspect ratio of trenches and vias. The wave form can be direct current (DC), pulse current (PC) or pulse reverse current (PRC).

[0032] In studies performed using 67 g/l of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 170 g/l of H_2SO_4 and 45 g/l of C1 as the starting bath, good plating results were obtained using a current density of 3.2 mA/cm² and 25.5 mA/cm² with DC, PC or PRC wave form. The following additive combinations produced the best results regarding trench filling:

Plating Solution	Composition (ppm)
1	C1(20) B1(12) L1(15)
2	C1(20) B1(12) L2 (25)
3	C1(20) B1(12) L3(25)
4	C1(20) B1(12) L4(25)

whereas:

C1 is polyethylene glycol

B1 is 3-mercapto-1-propanesulphonic acid sodium salt

L1 is poly(diallyldimethylammonium chloride)

L2 is diethylenetriamine

L3 is (R)-(-)-thiazoline-4-carboxylic acid

L4 is poly[bis(2-chloroethyl)ether-alt-1,3-bis[3-(dimethyl amino)propyl]urea, quaternized, 62 wt. % in water.

Claims

1. An acid copper electroplating composition comprising an aqueous solution of an acid and a copper salt, wherein at least one carrier compound, a water-soluble, mercapto-containing organic brightener compound and a leveller compound which comprises an organic compound containing single or multiple charged centres are present.

2. A composition according to Claim 1 in which the carrier compound is one or more of a polysaccharide compound, polyethylene glycol and poly(ethylene oxide).

3. A composition according to Claim 1 or Claim 2 in which the water-soluble, mercapto-containing organic brightener is one or more of N-methylallyl-N'-methylthiourea; tetramethylthiuram disulphide; ethylethylthiomethyl sulphoxide; ammonium diethyldithiocarbamate; dimethyl-2-thioxo-1,3-dithiole-4,5-dicarboxylate; 3-mercapto-1-propanesulphonic acid sodium salt; 3-mercapto-1-propanesulphonic acid; bis (2-mercaptoethyl) sulphide; ethylene trithio carbonate; ethanethiol; 2-mercaptoethanol; monothioglycerol (1-thioglycerol); 1,2-ethanedithiol; and thiodiethanol.

4. A composition according to any preceding claim in which the leveller is one or more of polymeric lev-

ellers, low molecular weight levellers and organic dyes.

5. A composition according to Claim 4 in which the polymeric leveller is one or more of polyethylenimine, 80% ethoxylated; poly(allylamine); poly(allylamine hydrochloride); polyaniline, sulphonated, 5 wt. % in water, 75 mole % sulphonated; poly[bis(2-chloroethyl)ether-alt-1,3-bis[3-(dimethylamino)propyl]urea, quaternized; poly[N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-1,6-hexanediamine-co-2,4-dichloro-6-morpholino-1,3,5-triazine; polyacrylamide; poly(acrylamide-co-diallyldimethylammonium chloride); poly(diallyldimethylammonium chloride); poly(melamine-co-formaldehyde), partially methylated; poly(4-vinylpyridine), 25% cross-linked; poly(1,2-dihydro-2,2,4-trimethylquinoline).

6. A composition according to Claim 4 in which the low molecular weight leveller is selected from the group consisting of: 2,5-dithiobiurea, dithioxamide, 1-phenyl-2-thiourea, diethylenetriamine; p-xylenebis(tetrahydrothiophenium) chloride, 2-thiohydantoin, pseudo thiohydantoin, (R)-(-)-thiazolidine-4-carboxylic acid, 3-(2'-thiopyridinium) propyl sulphate, 2,2'-dipyridyl disulphide, 4,4'-dipyridyl disulphide, thionicotinamide, 4-(trifluoromethyl)-2-pyrimidinethiol, 2-mercapto-4-methylpyrimidine hydrochloride, 5-phenyl-1 H-1,2,4-triazole-3-thiol, 5-(4'-pyridyl)-1 H-1,2,4-triazole-3-thiol, 2-amino-6-purinethiol, 4-amino-5-(4'-pyridyl)-4 H-1,2,4-triazole-3-thiol, diethyl heptadecyl imidazolinium ethylsulphate, hexamethylenetetraamine, 1,3-bis(3-pyridylmethyl)-2-thiourea, 2,4-diamino-6-mercaptopyrimidine hemisulphate, dithiouracil, 4,5-diamino-2,6-dimercaptopyrimidine, 4,5-diamino-6-hydroxy-2-mercaptopyrimidine hemisulphate hydrate, 4(5)-imidazoledithio-carboxylic acid, 2-mercapto-5-benzimidazolesulphonic acid, sodium salt dihydrate, 2-thiouracil, trithio cyanuric acid; (2-pyrimidylthio) acetic acid; 7-trifluoromethyl-4-quinlinethiol; 5-carbethoxy-2-thiouracil, 1 H-1,2,4-triazole-3-thiol; 1-phenyl-1 H-1,2,4-triazole-5-thiol, N, N'-ethylene thiourea, and 2-mercapto benzothiazole.

7. A composition according to Claim 4 in which the organic dye leveller is one or more of Bismarck Brown Y, Chicago Sky Blue 6B and Acid Violet.

8. A composition according to any preceding claim including a brightener/carrier species.

9. A composition according to any preceding claim including a carrier/leveller species.

10. A composition according to any preceding claim in which the weight ratio of carrier to leveller to bright-

ener ranges from about 0.09 to 47.6 : 0.09 to 47.6 :
0.2 to 4.7 weight/weight percent.

11. A method for copper plating of advanced interconnects comprising immersing the interconnects in a copper plating bath composition as claimed in any one of Claims 1 to 10.

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(54) **Electroplating solutions**

(57) An acid copper electroplating composition comprising an aqueous solution of an acid and a copper salt, wherein at least one carrier compound, a water-soluble, mercapto-containing organic brightener com-

pound and a leveller compound which comprises an organic compound containing single or multiple charged centres are present.

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The present search report has been drawn up for all claims.			
Place of search THE HAGUE		Date of completion of the search 23 October 2003	Examiner Gault, N
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document</p> <p>T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document</p>			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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